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LLNL-PROC-402330

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March 17, 2008

Nanotech 2008
Boston, MA, United States
June 1, 2008 through June 5, 2008

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ABSTRACT

To simulate polymer flows in microscale environments we have developed a numerical method that couples stochastic particle dynamics with an efficient incompressible Navier-Stokes solver. Here, we examine the convergence properties of the stochastic particle solver alone, and demonstrate that it has second order convergence in both weak and strong senses, for the examples presented.

Keywords: stochastic particle dynamics, RATTLE, particle-fluid coupling

1 INTRODUCTION

The dynamics of a continuum fluid with discrete embedded polymers is important for certain microfluidic applications, (e.g., so-called lab-on-a-chip PCR reactors) and for modeling viscoelastic phenomena in the dilute limit. Toward this end we proposed a fluid-particle coupling strategy [7] that uses Brownian dynamics to approximate molecular-level fluid–polymer interactions. In subsequent work (e.g., [3]) the time-stability of the scheme was improved, and constraints such as the non-crossing constraint for polymer-polymer interaction were considered. In this short paper we address the accuracy of our scheme, which has not been previously reported. We work here in the framework of a freely-jointed chain (no polymer-polymer interactions), we consider the fluid velocity field to be prescribed, and we do not consider any rigid domain boundaries. In the context of rigid constraint dynamics (*vs.* soft penalty method constraints) these omitted interactions will diminish the order of the local discretization error.

Recently, [8] proposed a weak second-order stochastic particle dynamics approach that is broadly similar to ours as described in [7], [3]. Our approach differs from theirs in our handling of the fluid–particle coupling, and our use of a Duhamel type discretization that recovers certain limiting behavior, thereby permitting longer stable time steps. In this paper we show that our approach is not only weak second-order accurate, but also second-order strong.

We model a polymer as a collection of coupled point masses, each subject to the Langevin equation of motion

$$m_\alpha \ddot{\mathbf{x}}_\alpha = m_\alpha \gamma(\mathbf{u} - \dot{\mathbf{x}}_\alpha) + \mathbf{F}(\mathbf{x}_\alpha) + \sigma \boldsymbol{\xi}_\alpha(t). \tag{1}$$

Here $\mathbf{x} = \mathbf{x}(t)$ is the position of αth particle with mass m_α, $\mathbf{u}$ is fluid velocity, $\mathbf{F}(x)$ is the interparticle force, $\gamma > 0$ the friction coefficient and $\boldsymbol{\xi}(t)$ is a white noise representing stochastic thermal bombardment by the solvent. The constant σ is given by $\sqrt{2m_\alpha \gamma k_B T}$ with k_B being Boltzmann's constant and T the temperature. The stable numerical integration of (1) can require a very small time step, especially in a highly viscous fluid where the relaxation time $1/\gamma$ can be vanishingly small.

In this work we will use Kramers' freely-jointed polymer model, which represents a polymer as point masses governed by (1) with the interparticle force $\mathbf{F}$ chosen to enforce the constraint of fixed interparticle spacing. The general idea is to add into equations of motion constraint forces that can be expressed as

$$\mathbf{G}_\alpha = -\sum_\beta \lambda_{\alpha\beta}(t) \nabla_\alpha \theta_{\alpha\beta} \tag{2}$$

$$\theta_{\alpha\beta} = \|\mathbf{x}_\alpha - \mathbf{x}_\beta\|^2 - a^2 = 0 \tag{3}$$

where particles of index β are neighbors of particle α, and $\lambda_{\alpha\beta}$ are Lagrange multipliers chosen to satisfy the constraints, and a =const. is the spacing between adjacent particles. This is usually performed by applying the SHAKE algorithm [5] or its velocity version RATTLE [1]. The fluid velocity $\mathbf{u}$ can be determined from a form of the incompressible Navier-Stokes equations with a particle coupling term [7]. For the purpose of developing the particle solver, we will take $\mathbf{u}$ as prescribed.

2 NUMERICAL METHOD

A numerical method for the integration of (1) was given without proof in [7]. Here, the derivation of those equations is given. We begin by expressing the second-order SDE as a system of first-order equations:

$$\begin{aligned} d\mathbf{x}(t) &= e^{-\gamma t}\mathbf{z}(t)dt \\ d\mathbf{z}(t) &= \gamma e^{\gamma t}\mathbf{u}(t, \mathbf{x}(t))dt + \frac{\sigma}{m} e^{\gamma t} d\mathbf{W}, \end{aligned} \tag{4}$$

and

$$\mathbf{x}(t) = \mathbf{x}(0) + \int_0^t e^{-\gamma s}\mathbf{z}(s)ds \tag{5}$$

$$\mathbf{z}(t) = \mathbf{z}(0) + \int_0^t \gamma e^{\gamma s}\mathbf{u}(s,\mathbf{x}(s))ds + \int_0^t \frac{\sigma}{m}e^{\gamma s}d\mathbf{W}_s$$

where $\mathbf{z} = \mathbf{v}e^{\gamma t}$, $\mathbf{W}(t)$ is a standard Weiner process, and $d\mathbf{W} = \boldsymbol{\xi}dt$.

We then expand our equations of motion in an Itô-Taylor series, using the Itô calculus for stochastic ODEs [2]:

$$\begin{aligned} &Y = U(t,X(t)) \\ &dX(t) = f(t)dt + g(t)dW \\ &dY(t) = \left[\frac{\partial U}{\partial t} + \frac{\partial U}{\partial X}f(t) + \frac{1}{2}\frac{\partial^2 U}{\partial X^2}g^2(t)\right]dt + \frac{\partial U}{\partial X}gdW. \end{aligned} \tag{6}$$

Application of this stochastic chain rule requires care to account for all dependence on stochastic variables. In real systems, the fluid $\mathbf{u}$ is driven by a nonlinear stochastic coupling (see (**??**)). Additionally, every fluid element undergoes thermal fluctuation, whether expressed explicitly as a Brownian force or not. However, the average magnitude of such fluctuations in a given volume scales as the inverse of the number of atoms in that volume. At the scales of length with which we are concerned, the continuum fluid motion $\mathbf{u}$ is smooth. Thus, in our analysis, the stochastic dependence of $\mathbf{u}$ is through the particle position $\mathbf{x}$ only: $\mathbf{u} = \mathbf{u}(t,\mathbf{x}(t))$.

With this assumption, application of the Itô formula to the $\mathbf{W}$-dependent integrands of (5) gives

$$\begin{aligned} e^{-\gamma s}\mathbf{z}(s) &= \mathbf{z}(0) + \int_0^s \Big[-\gamma e^{-\gamma s_1}\mathbf{z}(s_1) + \\ &\qquad \gamma\mathbf{u}(s_1,\mathbf{x}(s_1))\Big]ds_1 + \frac{\sigma}{m}\int_0^s d\mathbf{W}_{s_1} \\ \gamma e^{\gamma s}\mathbf{u}(s,\mathbf{x}(s)) &= \gamma\mathbf{u}(0,\mathbf{x}(0)) + \int_0^s \Big[\gamma^2 e^{\gamma s_1}\mathbf{u}(s_1,\mathbf{x}(s_1)) \\ &\qquad + \gamma e^{\gamma s_1}\frac{D\mathbf{u}(s_1,\mathbf{x}(s_1))}{Ds_1}\Big]ds_1. \end{aligned} \tag{7}$$

Substituting expansions (7) into (5) gives

$$\begin{aligned} \mathbf{x}(t) &= \mathbf{x}(0) + t\mathbf{z}(0) + \int_0^t\int_0^s \Big[-\gamma e^{-\gamma s_1}\mathbf{z}(s_1) + \\ &\qquad \gamma\mathbf{u}(s_1,\mathbf{x}(s_1))\Big]ds_1 ds + \frac{\sigma}{m}\int_0^t\int_0^s d\mathbf{W}_{s_1}ds \\ \mathbf{z}(t) &= \mathbf{z}(0) + \gamma t\mathbf{u}(0,\mathbf{x}(0)) + \int_0^t\int_0^s \Big[\gamma^2 e^{\gamma s_1}\mathbf{u}(s_1,\mathbf{x}(s_1)) + \\ &\qquad \gamma e^{\gamma s_1}\frac{D\mathbf{u}(s_1,\mathbf{x}(s_1))}{Ds_1}\Big]ds_1 ds + \frac{\sigma}{m}\int_0^t e^{\gamma s}d\mathbf{W}_s \end{aligned} \tag{8}$$

where $\frac{D}{Dt} = \frac{\partial}{\partial t} + (\mathbf{v}(t)\cdot\nabla) = \frac{\partial}{\partial t} + e^{-\gamma t}(\mathbf{z}(t)\cdot\nabla)$ is the material derivative. Applying the Itô formula (6) again, now to the integrands of (8), gives, after simplification,

$$\begin{aligned} &\mathbf{x}(t) = \mathbf{x}(0) + t\mathbf{z}(0) + \frac{\gamma t^2}{2}[\mathbf{u}(0,\mathbf{x}(0)) - \mathbf{z}(0)] + \\ &\qquad \gamma\int_0^t\int_0^s\int_0^{s_1}\Big[\frac{D\mathbf{u}(s_2,\mathbf{x}(s_2))}{Ds_2} + \gamma e^{-\gamma s_2}\mathbf{z}(s_2) - \\ &\qquad \gamma\mathbf{u}(s_2,\mathbf{x}(s_2))\Big]ds_2 ds_1 ds + \frac{\sigma}{m}\int_0^t\int_0^s d\mathbf{W}_{s_1}ds \\ &\qquad -\gamma\frac{\sigma}{m}\int_0^t\int_0^s\int_0^{s_1} d\mathbf{W}_{s_2}ds_1 ds_2 \\ &\mathbf{z}(t) = \mathbf{z}(0) + \gamma t\mathbf{u}(0,\mathbf{x}(0)) + \frac{t^2}{2}[\gamma^2\mathbf{u}(0,\mathbf{x}(0)) + \\ &\qquad \gamma\frac{D\mathbf{u}(0,\mathbf{x}(0))}{Dt}] + \int_0^t\int_0^s\int_0^{s_1}\Big[\gamma^3 e^{\gamma s_2}\mathbf{u}(s_2,\mathbf{x}(s_2)) + \\ &\qquad 2\gamma^2 e^{\gamma s_2}\frac{D\mathbf{u}(s_2,\mathbf{x}(s_2))}{Ds_2} + \gamma e^{\gamma s_2}\frac{D^2\mathbf{u}(s_2,\mathbf{x}(s_2))}{Ds_2^2}\Big]ds_2 ds_1 ds \\ &\qquad +\frac{\sigma\gamma}{m}\int_0^t\int_0^s\int_0^{s_1}(\nabla\mathbf{u}(s_2,\mathbf{x}(s_2)))\cdot d\mathbf{W}_{s_2}ds_1 ds \\ &\qquad +\frac{\sigma}{m}\int_0^t e^{\gamma s}d\mathbf{W}_s. \end{aligned} \tag{9}$$

In the notation of [2], repeated application of the Itô chain rule to the $\mathbf{x}$ equation will give rise to multiple integrals of the form

$$\begin{aligned} I_{(1,0)} &= \int_0^t ds_0\int_0^{s_0} dW_{s_1} \\ I_{(1,0,0)} &= \int_0^t ds_0\int_0^{s_0} ds_1\int_0^{s_1} dW_{s_2} \\ &\cdots \\ I_{(\underbrace{1,0,...,0}_{n\text{ terms}})} &= \int_0^t ds_0\int_0^{s_0} ds_1 ...\int_0^{s_{n-2}} dW_{s_{n-1}}. \end{aligned} \tag{10}$$

It can be shown [2, proposition 5.2.3] that

$$\begin{aligned} I_{(1,0)} &= \int_0^t (t-s)dW_{s_0} \\ I_{(1,0,0)} &= \frac{1}{2}\int_0^t (t-s)^2 dW_{s_0} \\ &\cdots \\ I_{(\underbrace{1,0,...,0}_{n\text{ terms}})} &= \frac{1}{(n-1)!}\int_0^t (t-s)^{n-1}dW_{s_0}. \end{aligned} \tag{11}$$

It follows that repeated application of the Itô chain rule to the $\mathbf{x}$ equation will converge to a single stochastic integral

$$\frac{\sigma}{\gamma m}\int_0^t \left[1 - e^{-\gamma(t-s)}\right]dW_s. \tag{12}$$

The Itô-Taylor series expansion therefore gives the effective stochastic position and velocity terms

$$\mathbf{R}_x = \frac{1}{\gamma}\int_0^t \left[1 - e^{-\gamma(t-s)}\right]d\mathbf{W}_s \tag{13}$$

$$\mathbf{R}_v = \int_0^t e^{-\gamma(t-s)}d\mathbf{W}_s \tag{14}$$

with zero mean and variances:

$$\begin{aligned} E(\mathbf{R}_x \otimes \mathbf{R}_x) &= \mathbf{I}\int_0^t \frac{[1-e^{-2\gamma(t-s)}]^2}{\gamma^2} ds \\ &= \mathbf{I}\frac{2\gamma t - e^{-2\gamma t} - 4e^{-\gamma t} - 3}{2\gamma^3} \\ E(\mathbf{R}_v \otimes \mathbf{R}_v) &= \mathbf{I}\frac{1-e^{-2\gamma t}}{2\gamma} \\ E(\mathbf{R}_x \otimes \mathbf{R}_v) &= \mathbf{I}\frac{(e^{-\gamma t}-1)^2}{2\gamma^2}. \end{aligned} \tag{15}$$

Numerically, these stochastic terms are constructed by assuming $\mathbf{R}_v = \sqrt{E(R_v^2)}\mathbf{U}_1$, where $\mathbf{U}_1$ is a vector of uniform standard deviates. Then, $\mathbf{R}_x$ is given by $\mathbf{R}_x = a\mathbf{U}_1 + b\mathbf{U}_2$, where $\mathbf{U}_2$ is an independent vector of uniform deviates, and constants a and b are

$$\begin{aligned} a &= \frac{1}{\gamma}\tanh\left(\frac{\gamma t}{2}\right)\sqrt{\frac{1-e^{-2\gamma t}}{2\gamma}} \\ b &= \frac{1}{\gamma}\sqrt{t - \frac{2}{\gamma}\tanh\left(\frac{\gamma t}{2}\right)} \end{aligned} \tag{16}$$

in order that $\mathbf{R}_v$ and $\mathbf{R}_x$ obey (15).

Taking into account all of the above, and truncating high order terms, we can write our integral equations of motion as

$$\begin{aligned} \mathbf{x}(t+\tau) &= \mathbf{x}(t) + [\mathbf{v}(t) - \mathbf{u}(t,x(t))]\frac{1-e^{\gamma\tau}}{\gamma} + \\ &\quad \mathbf{u}(t,\mathbf{x}(t))\tau + \frac{\sigma}{m}\mathbf{R}_x \\ \mathbf{v}(t+\tau) &= \mathbf{v}(t)e^{-\gamma\tau} + \mathbf{u}(t,\mathbf{x}(t))(1-e^{-\gamma\tau}) + \frac{\sigma}{m}\mathbf{R}_v \end{aligned} \tag{17}$$

where τ is a time step of approximation. These discrete integral equations correspond exactly to the analytical solution under the assumption of no stochastic force, and constant uniform $\mathbf{u}$. The recovery of this exact limit through the Duhamel form is the principal advantage of our method, enabling $\tau\gamma \gg 1$. In applications with varying $\mathbf{u}$, we use a predictor-corrector formalism ([7]) to time-center the evaluation of $\mathbf{u}$ on particle paths.

By the theorem of [4], the omission of stochastic terms $\mathcal{O}(\tau^{5/2})$ and deterministic terms $\mathcal{O}(\tau^3)$ in our velocity equation gives a theoretical order of accuracy of 2 strong and 2 weak.

Adding constraint forces into our integrator (17) leads to the following

$$\begin{aligned} \mathbf{x}(t+\tau) &= \mathbf{x}(t) + [\mathbf{v}(t) - \mathbf{u}(t,x(t))]\frac{1-e^{\gamma\tau}}{\gamma} + \\ &\quad \mathbf{u}(t,\mathbf{x}(t))\tau + \frac{\sigma}{m}\mathbf{R}_x + \frac{1}{m}\mathbf{G}(\mathbf{x}(t)) \qquad (18) \\ \mathbf{v}(t+\tau) &= \mathbf{v}(t)e^{-\gamma\tau} + \mathbf{u}(t,\mathbf{x}(t))(1-e^{-\gamma\tau}) + \frac{\sigma}{m}\mathbf{R}_v \\ &\quad + \frac{1}{m}\frac{1}{\tau}\left[\mathbf{G}^*(\mathbf{x}(t+\tau)) + \mathbf{G}(\mathbf{x}(t))\right] \qquad (19) \end{aligned}$$

Table 1: Weak approximation error and rate of convergence.

$2\tau/\tau$	error	rate
256/128	6.25E-13	2.54
128/64	3.63E-12	2.01
64/32	1.46E-11	1.85
32/16	5.24E-11	2.03
16/8	2.14E-10	1.98
8/4	8.47E-10	

where $\mathbf{G}(\mathbf{x}(t))$ and $\mathbf{G}^*(\mathbf{x}(t+\tau))$ are given by (2). Here, Lagrange multipliers $\lambda_{\alpha\beta}$ in (18) are chosen so that

$$\theta_{\alpha\beta}(\mathbf{x}(t)) = \|\mathbf{x}_\alpha - \mathbf{x}_\beta\|^2 - a^2 = 0 \tag{20}$$

and $\lambda^*_{\alpha\beta}$ in (19) are chosen so that

$$\dot{\theta}_{\alpha\beta}(\mathbf{x}(t+\tau)) = (\dot{\mathbf{x}}_\alpha - \dot{\mathbf{x}}_\beta)\cdot(\mathbf{x}_\alpha - \mathbf{x}_\beta) = 0. \tag{21}$$

The Lagrange multipliers are determined by the `RATTLE` algorithm [1]. See also [8].

3 RESULTS AND CONCLUSIONS

The calculation uses run parameters $\gamma = 10^{10}$/s, $m_\alpha = 2.0\times10^{-18}$kg, $a = 7.0\mu$m, which correspond with lambda-phage DNA subdivided into Kuhn length segments. The velocity field is $u_i = 10^{-3}\cos(10^3 x_i)$.

Because the exact solution is not accessible we define the error as the difference of successive solutions

$$\mathrm{E}(\|r_\alpha^{(2\tau/\tau)}\|) = \mathrm{E}(\|\mathbf{x}_\alpha^{(2\tau)} - \mathbf{x}_\alpha^{(\tau)}\|), \tag{22}$$

and rate of convergence as

$$k = \log_2\left(\frac{\mathrm{E}(\|\mathbf{r}_\alpha^{(4\tau/2\tau)}\|)}{\mathrm{E}(\|\mathbf{r}_\alpha^{(2\tau/\tau)}\|)}\right), \tag{23}$$

where superscript (τ) denotes the time step used.

The results of our numerical computations, presented in Figs. 1&2 and Tables 1&2, suggest that the rate of convergence is indeed second order weak and second order strong for the examples used. (The strong order assessment does not include constraints.) The weak error is measured by measuring the error after averaging over paths; the strong error is the path-wise average error. Calculation is made for a 6-bead polymer, for time $T = 10^{-2}$. We measure the error in the final coordinate of particle $\alpha = 2$ in the chain. Averaging is performed over 10^4 independent paths. E_1, E_2 and E_∞ in Fig. 2 and Table 2 refer to different norms [6].

Work to assess the strong order of convergence with constraint forces is in progress.

Table 2: Strong approximation error E_1, E_2, E_∞ and rate of convergence, without constrains.

$2\tau/\tau$	error E_1	rate E_1	error E_2	rate E_2	error E_∞	rate E_∞
256/128	8.58E-13	1.96	8.73E-13	1.94	1.50E-12	1.61
128/64	3.34E-12	1.99	3.35E-12	1.98	4.56E-12	1.80
64/32	1.32E-11	2.00	1.33E-11	2.00	1.59E-11	1.85
32/16	5.29E-11	2.00	5.29E-11	2.00	5.73E-11	1.96
16/8	2.11E-10	2.00	2.11E-10	2.00	2.23E-10	1.96
8/4	8.46E-10		8.46E-10		8.68E-10	

Figure 1: Weak error.

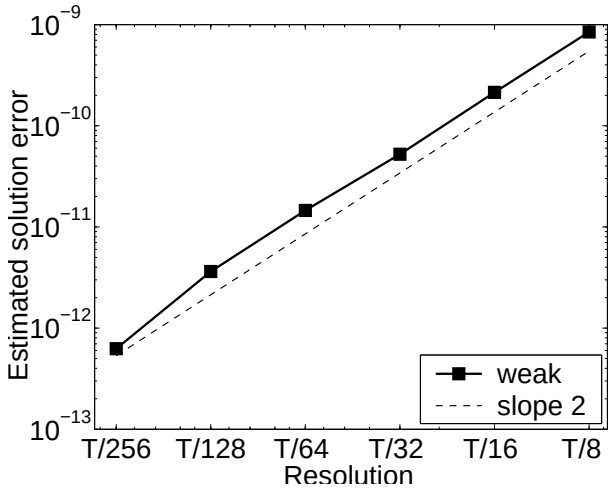
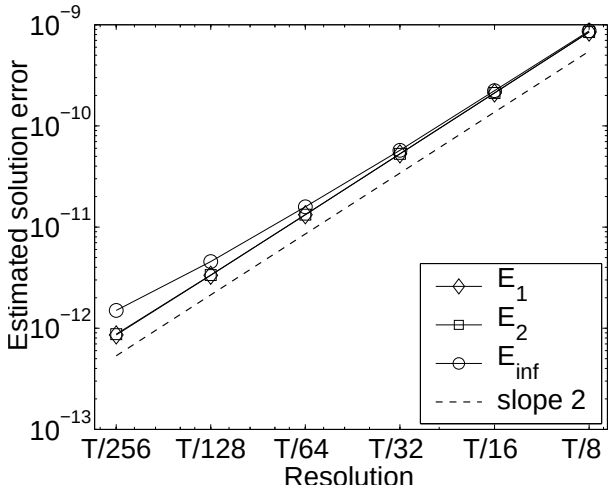


Figure 2: Strong error (no constraints).



ACKNOWLEDGMENT

B. Kallemov was supported by the Bolashak scholarship of the President of the Republic of Kazakhstan. G. H. Miller was supported by LLNL IUT subcontracts number B550201 and number B553964, and by DOE MICS contract number DE-FG02-03ER25579. Work at LLNL was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract DE-AC52-07NA27344.

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